

# PATENT SPECIFICATION

(11) 1 465 046

1 465 046

- (21) Application No. 22783/73 (22) Filed 14 May 1973  
 (21) Application No. 44131/73 (22) Filed 20 Sept. 1973  
 (23) Complete Specification filed 16 April 1974  
 (44) Complete Specification published 16 Feb. 1977  
 (51) INT CL<sup>2</sup> C08K 5/53; C08J 3/20 (C08K 5/53, 3/22, 5/09)  
 (52) Index at acceptance  
 C3R 22C C10 C11 C12 C13M C13P C16 C29 C4 C5B1  
 C5B2 C6B C6X C8P L1B L2C1 L3A L3B L5B  
 L6D L6F



(72) Inventors JIRI TOMKA and JACK MACILWAIN GINN

## (54) IMPROVED POLYAMIDE COMPOSITION

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to nucleated polyamides exhibiting an increased rate of crystallisation and to processes for the preparation thereof.

It is known to employ nucleating agents to improve the properties of moulded polyamides, in particular by imparting a fine-grained uniform structure resulting in the article being substantially stress-free. In addition, due to the increased rate of crystallisation, nucleating agents substantially shorten the injection moulding cycle time, thus increasing productivity.

Some nucleated polyamides, e.g. 66 nylon, exhibit improved productivity when spun into fibres compared with the unnucleated polyamide as described in British Patent Specification No. 1211685.

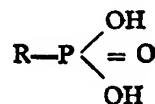
In the processes for the preparation of such nucleated polyamides finely divided solid materials which give a nuclei-forming effect are added to the polyamide and uniformly dispersed therethrough.

British Patent No. 851300 discloses, as nucleating agents, materials such as graphite, molybdenum disulphide, cobalt and ferrous sulphides, tungsten sulphide, Scheelite, alkali metal halides such as lithium fluoride and silicic acid, in amounts ranging from 0.001 to 0.1% by weight.

British Patent No. 889403 describes the use of 0.1 to 1% by weight of the metal salt of a saturated or unsaturated fatty acid to induce nucleation. The metal may be calcium, magnesium, zinc, lithium, sodium, potassium, cadmium, aluminium or lead and the fatty acids stearic, oleic or palmitic acids. The use of these materials may be employed not only with polyamides but also with polyurethane

or polyethylene polymers. It has now been found that metal salts such as salts of carboxylic acids give an improved nucleating effect when used in combination with organo-phosphonic acids.

According to the invention there is provided a method of producing a polyamide composition comprising intimately blending an organophosphonic acid or derivative thereof of general formula



where R is a hydrocarbyl radical and a metal compound which is a metal salt of a saturated or unsaturated carboxylic acid, a metal oxide or hydroxide with a polyamide under melt conditions wherein the metal is selected from Groups 2a, 2b, 3b, 4b, 7a and 8 of the Periodic Table of Elements (as tabulated on page 30 of Advanced Inorganic Chemistry by Cotton and Wilkinson published in 1962 by Interscience Publishers) and wherein either the metal compound or the organo-phosphorus compound, but not the combination of both compounds, may have been present during the polymerisation of the polyamide.

The compositions produced by such a method shows a rapid crystallisation rate enabling, for example, an increased rate of production of polyamide articles moulded from the composition to be obtained.

The term "organo-phosphonic acid" as used herein includes any derivative of said acid which under the reaction conditions involved during the melt blending process will react with the metal compound to produce the same effect as the free acid.

The desired blending may be achieved by a variety of methods. For example, the specified metal salts, oxides or hydroxides may be introduced into molten polyamides containing the organo-phosphonic acid. Alternatively, the organo-phosphonic acid can be incorporated

50

55

60

65

70

75

80

85

into molten polymer already containing the source of metal, or both components can be incorporated simultaneously into molten polyamide.

5 Whatever blending process is used it is necessary that the metal compound and the organo-phosphorus compound are mixed together in the polyamide when it is in a molten state, for example during melt extrusion of the polyamide from an extruder. If both the types of compound are brought together during the polymerisation of the polyamide whilst the reactants are present in solution form the beneficial increase in crystallisation rate obtained from the products derived from the present invention is not observed.

10 The two types of compound may each be added to separate batches of polyamide during the polymerisation of the polyamide and these batches may subsequently be melt blended to give a product having the advantage conferred by the present invention but it is preferred that the metal compound is not introduced during a polymerisation stage because such materials can cause chain transfer with the result that low molecular weight polyamides are produced. For this reason it is preferred that the metal compound is blended with polyamide after the polymerisation of the polyamide. On the other hand the organo-phosphonic acids may generally be added to the polymerisation reactants without adverse effect and this is a preferred method of blending the organo-phosphonic acid with the polyamide.

35 A convenient method of intimately blending the components together is by a masterbatch technique in which one or more of one type of the combination of additive materials is first incorporated at a relatively high concentration into the polyamide and the resulting material is then compounded with further polyamide containing one or more of the other type of the combination to give the required concentration of ingredients in the final compound. Additional polyamide not containing either type of additive may be included to adjust concentrations to a desired level. Processes in which the additives of the combination are separately dispersed in batches of polyamides before melt blending together are preferred because these processes have been found to give rise to a greater increase in crystallisation rate for a given concentration of additives than processes which produce blends containing the same concentration of additives but in which one additive of the combination is added directly to a polyamide containing the other additive or in which both additives are dry blended together before addition to a molten polyamide. Similarly, the masterbatch technique of blending polymers already containing the additives permits the use of lower concentrations of additives than in the techniques

in which the additives are not first introduced into separate batches of the polyamide.

The addition of preformed metal salts of the organo-phosphonic acids specified to a molten polyamide does not give a composition having the improved crystallisation behaviour of products produced by the present invention.

70 Polyamides in which the present invention may be usefully employed include those derived from lactams or omega-amino carboxylic acids, such as poly-epsilon-caprolactam or polyaminoundecanoic acid or from the salts of diamines and dicarboxylic acids such as polyhexamethylene adipamide. The polyamides may, in addition to the combination of nucleating additives of the present invention, also contain the usual additives such as delustrants, brightening agents, stabilisers against the action of heat and light, fillers or dyestuffs. When required for non-fibre application, for example, the polyamide may also contain toughening agents, for example ethylene-vinyl acetate copolymers. In particular, the polyamide may contain a reinforcing agent—for example glass fibres, glass ballotini or mica. These additives may be present in an amount from 5% up to about 60% by weight of the polyamide. Flame retardant agents may also be present, for example, those disclosed in our British Patent No. 1208865.

85 Suitable organo-phosphonic acids include both cycloaliphatic and aromatic (including aralkyl) phosphonic acids or corresponding derivatives thereof, for example, halides and esters derived from the acids. Under the severe reaction conditions involved during the melt blending processes such derivatives react with the metal compounds to give the same effect as the free acids. Preferred compounds are cyclohexyl, phenyl and benzyl phosphonic acids or derivatives such as phenyl phosphonic dichloride and dimethyl phenyl phosphonate. Their concentration should preferably be such as to give 0.15 mole of phosphorus per 10<sup>6</sup> g of the resulting composition although concentrations as low as 0.025 mole of phosphorus per 10<sup>6</sup> g show a significant nucleating effect. Concentrations above 120 mole phosphorus per 10<sup>6</sup> g are impractical. The most preferred concentration rate is 0.3—20 mole phosphorus per 10<sup>6</sup> g.

100 The metal salts of saturated or unsaturated carboxylic acids, metal oxides and hydroxides include aluminium, zinc, magnesium, calcium, barium, cadmium and manganese. The metals of group 8 of the Periodic Table, e.g. cobalt and nickel, are also suitable but give rise to undesirably coloured products. They may be used in applications which can tolerate this colour. The carboxylic acids include acetic, stearic and oleic acids.

105 It is advantageous to employ salts having a low melting temperature, viz below the pro-

70

75

80

85

90

95

100

105

110

115

120

125

130

cessing temperature of the polyamide.

The molar concentration range of metals is similar to that for phosphorus as defined above.

It is known from British Patent No. 928286 to use zinc salts of saturated or unsaturated fatty acids together with an inorganic oxy-acid of phosphorus or a salt thereof for the purpose of stabilising the melt viscosity of polyamides. However, such combinations do not have the nucleating activity in polyamides as do the combinations of the present invention using organo-phosphorus acids.

The compositions of the present invention are also suitable for melt extrusion by conventional techniques to form films which crystallise at higher temperatures than would films derived from unnucleated polyamide. The high efficiency of the present systems, permits a useful effect to be obtained using low concentrations of additives. This is particularly useful in films for food applications where the presence of additives should be kept to a minimum.

The rate of crystallisation and thus the efficiency of nucleation, are conveniently assessed by a DSC technique; molten polymer is cooled at constant rate and in certain temperature range the crystallisation is observed as an exotherm. The onset of the crystallisation peak ( $T_c$ ) and the crystallisation peak temperature ( $T_p$ ) are related to the crystallisation rate. The values  $T_c$  and  $T_p$  depend upon melting conditions and also upon cooling rate  $q_c$ . The melting temperature ( $T_m$ ) of the polymer may also be observed from the heating cycle.

The results given in the examples were obtained by using Perkin Elmer DSC 1B

apparatus, for 66 nylon the conditions were as follows: heating rate  $16^\circ\text{C}/\text{min}$ , holding 3 mins at  $300^\circ\text{C}$ , cooling rate  $q_c$  of either  $16^\circ\text{C}$  or  $64^\circ\text{C}/\text{min}$ , weight of sample was 8 mg.

It is preferred that the polyamide compositions resulting from the method of the invention should show a crystallisation peak temperature, measured under these conditions using a cooling rate of  $16^\circ\text{C}/\text{min}$  of at least  $2^\circ\text{C}$  greater than the polyamide not treated by the method of the invention.

The invention will now be further described by reference to the following illustrative and comparative examples.

#### EXAMPLE 1.

Granules of 66 nylon polymer having a relative viscosity of 44 (measured at  $25^\circ\text{C}$  in a solution containing 5.5 g polymer in 50 mls of 90% formic acid) and containing 0.15% w/w  $\text{TiO}_2$  and 0.25% w/w cyclohexyl phosphonic acid ( $15.2 \mu\text{ mole P/g}$ ) were coated with measured quantities of zinc stearate or zinc acetate and the mixtures were passed through a horizontal screw extruder at a temperature  $285\text{--}290^\circ\text{C}$ . The extruded lace of circular cross-section was quenched in a bath of cold water and cut into cylindrical granules. The granules were dried in vacuum at  $90\text{--}100^\circ\text{C}$  for 16 hours and the crystallisation behaviour was examined as described above. The results shown in Table 1 indicate that the temperatures for onset of crystallisation and the peak crystallisation temperatures are increased in the presence of the combination of the zinc salts and the cyclohexyl phosphonic acid showing that crystallisation both begin and are completed earlier in the cooling cycle than in the control run.

TABLE 1

Additive	Zn $\mu$ mole/g	$T_m$ (peak) $^\circ\text{C}$	$T_c$ $^\circ\text{C}$ $q_c=16^\circ\text{C}/\text{min}$	$T_p$ $^\circ\text{C}$ $q_c=16^\circ\text{C}/\text{min}$	$T_c$ $^\circ\text{C}$ $q_c=64^\circ\text{C}/\text{min}$	$T_p$ $^\circ\text{C}$ $q_c=64^\circ\text{C}/\text{min}$
None	0	265	235	228	218	205
Zn-stearate 0.23%	3.6	265	243	231	229	212
Zn-stearate 0.50%	7.9	265	246	236	232	217
Zn-stearate 1.0%	15.8	265	248	237	234	218
$(\text{CH}_3\text{COO})_2\text{Zn}$ $2\text{H}_2\text{O}$ , 0.35%	15.8	265	247	239	235	218

As further control experiments the crystallisation behaviour of the polymer (relative viscosity 44) without additives and containing

0.3% by weight of zinc stearate ( $4.7 \mu\text{ mole/g}$ ) was examined. The results are shown in the table below.

TABLE 2

Sample	Zn $\mu$ mole/g	T <sub>m</sub> (peak) °C	T <sub>c</sub> °C q <sub>c</sub> =16°C/min	T <sub>p</sub> °C	T <sub>c</sub> °C q <sub>c</sub> =64°C/min	T <sub>p</sub> °C
Nylon 66 only	0	265°	232	226	218	206
Nylon 66 - Zn stearate (0.3%)	4.7	265°	232	225	217	205

The results indicate that neither additive of the combination is effective alone in influencing the crystallisation behaviour of the polyamide.

#### EXAMPLE 2.

Granules of three 66 nylon polymers, A, B and C, containing A—0.15% w/w TiO<sub>2</sub>, 0.25% w/w cyclohexyl phosphonic acid (15.2

$\mu$  mole P/g), B—0.2% w/w ethylene-bis-stearamide, 0.3% w/w zinc stearate (4.7  $\mu$  mole zinc/g) and C—no additives and having relative viscosities 44, 40 and 42, respectively, were tumble blended and the mixtures were processed as described in Example 1. The crystallisation behaviour of the products was examined; results are given in Table 3.

TABLE 3

Composition, wt %			P $\mu$ mole/g	Zn $\mu$ mole/g	T <sub>m</sub> (peak) °C	T <sub>c</sub> °C q <sub>c</sub> =16°C/min	T <sub>p</sub> °C	T <sub>c</sub> °C q <sub>c</sub> =64°C/min	T <sub>p</sub> °C
A	B	C							
0	76.4	23.6	0	3.6	265	232	226	217	205
11.8	38.3	49.9	1.8	1.8	265	243	232	232	214
23.6	76.4	0	3.6	3.6	264	245	234	235	217
100.0	0	0	15.2	0	264	234	226	218	207

#### EXAMPLE 3.

A range of metal acetates was added to 66 nylon polymer having a relative viscosity 57 containing 0.20% w/w cyclohexyl phosphonic acid (12  $\mu$  mole P/g) by melt blending at 295°C for 15 mins. The crystallisation

behaviour of the product was studied using a cooling rate of 64°C/min. Details are shown in Table 4. The acetates were added in proportions to give 24  $\mu$  equiv. m/g where m = metal.

TABLE 4

Metal	T <sub>m</sub> (peak)	T <sub>c</sub> °C	T <sub>p</sub> °C
Magnesium (Mg <sup>++</sup> )	265	233	216
Calcium (Ca <sup>++</sup> )	263	233	217
Barium (Ba <sup>++</sup> )	263	223	209
Zinc (Zn <sup>++</sup> )	266	227	209
Cadmium (Cd <sup>++</sup> )	264	230	213
Manganese (Mn <sup>++</sup> )	264	232	216
Cobalt (Co <sup>++</sup> )	262	229	211
Nickel (Ni <sup>++</sup> )	258	220	209
Control (No metal)	260	207	192

**EXAMPLE 4.** Example 1 was repeated using metal stearate and a 66 nylon polymer containing 0.20% phenyl phosphonic acid (12  $\mu$  mole P/g). Details are given in Table 5.

TABLE 5

	Metals $\mu$ equiv/g	RV	T <sub>m</sub> (peak) °C	T <sub>c</sub> °C q <sub>c</sub> =16°/min	T <sub>p</sub> °C	T <sub>c</sub> °C q <sub>c</sub> =64°/min	T <sub>p</sub> °C
Mg stearate 0.42%	14	63.8	265	241	230	228	210
Ca stearate 0.44%	14	59.7	266	234	227	220	209
Al stearate 0.42%	14	53.2	264	240	229	228	212
ZnO 0.10% + Zinc stearate 0.30% + ethylene- b-stearamide 0.20%	34	51.4	264	243	231	230	213

**EXAMPLE 5.** 0.32 parts by weight of magnesium acetate tetrahydrate were dehydrated by heating it for 2 hours at 130—140°C under atmospheric pressure and the resultant powder tumble blended with 100 parts by weight of dry 66 nylon granulate containing 1.15% w/w TiO<sub>2</sub> and 0.25% w/w cyclohexyl phosphonic acid and having a relative viscosity of 44. The mixture was processed as described in Example 1. Crystallisation behaviour of the product was compared with that of original polymer. Results are given in Table 6.

TABLE 6

Material	T <sub>m</sub> (peak) °C	T <sub>c</sub> °C q <sub>c</sub> =16°/min	T <sub>p</sub> °C	T <sub>c</sub> °C q <sub>c</sub> =64°/min	T <sub>p</sub> °C
Original polymer	264	231	224	215	204
Nucleated composition	264	247	237	234	219

The original polymer, the nucleated composition and also additive-free control 66 nylon polymer (relative viscosity 43) were spun on a single end machine to 13-filament yarn at a spinning speed 1127 metres per minute.

Extensibility of spun yarns was tested using an "Instron" tensometer (deformation rate 1000%/min.). ("Instron" is a registered Trade Mark). Results are given in Table 7. The undrawn yarn prepared from the nucleated polymer also exhibited X-ray reflection patterns typical for undrawn yarns prepared from nucleated 66 nylon as described in British Patent No. 1211685.

Spun yarns were drawn to draw ratios specified in Table 7. Extensibility of drawn

yarns was measured using an Instron tensometer, deformation rate 100%/min. Productivity ratio PR was calculated using the following formula

$$PR = \frac{DR^s (\epsilon_B^s + 100)}{DR^c (\epsilon_B^c + 100)}$$

where DR is draw ratio and  $\epsilon_B$  is extensibility (%); superscript s indicates values obtained with experimental yarns, superscript c indicates values obtained with additive-free control yarn. Values given in Table 7 demonstrate that substantial increase in PR is observed in the case when the combination of cyclohexyl phosphonic acid and magnesium salt is present in the polymer used for spinning.

TABLE 7

Polymer	Spun Yarns			Drawn Yarns		
	dtex	Ext. %	Draw ratio	dtex	Ext. %	PR
Additive-free control	121	255	2.91	43	27.4	—
Original polymer	120	297	2.91	44	41.0	1.11
			3.17	40	28.5	1.10
Nucleated composition	120	423	2.91	44	75.3	1.30
			3.93	32	33.1	1.41

## EXAMPLE 6.

The following experiment demonstrates the improvement in crystallinity behaviour obtained when the components forming an active nucleant are brought together in a medium of high viscosity, namely in a molten polyamide, compared with the behaviour when the components are combined at the polymer making stage when the reactants are still in solution.

**Polymer A** — 7000 g of 66 salt, 3000 g of water and 5.18 g of magnesium acetate tetrahydrate were charged into a 16 litre autoclave and subjected to normal 66 nylon manufacturing process; during the polymerisation and whilst the reactants were still in solution

a solution of cyclohexyl phosphonic acid (3.9 g in 300 mls of water) was added. Prepared polymer was discharged, dried and its crystallisation behaviour was examined. Results are given in Table 8.

**Polymer B** — 0.16 parts by weight of magnesium acetate tetrahydrate were dehydrated by heating it for 2 hours at 130—140°C under atmospheric pressure and the resulted powder was blended with 100 parts by weight of dry 66 nylon granulate (containing 3.6  $\mu$  mole cyclohexyl phosphonic acid per gram and having relative viscosity of 57). The mixture was processed as described in Example 1 and the product was tested. The results are quoted in Table 8.

TABLE 8

Polymer	Relative viscosity	P $\mu$ mole/g	Mg g	T <sub>m</sub> (peak)	T <sub>c</sub> q <sub>c</sub> =64°/min	T <sub>p</sub> °min
A	38	4.0	4.0	263	220	207
B	50	3.6	3.7	264	231	216

## EXAMPLE 7.

Granules of 6.9 nylon polymer containing respectively a) no additive, b) 12.2  $\mu$  mole P/g cyclohexyl phosphonic acid (added to salt solution prior to polymerisation), c) material b) coated with magnesium acetate to give 12.2

$\mu$  mole M/g was extruded as described in Example 1 and the crystallisation behaviour examined as previously described. Relative viscosities of polymers and the crystallisation behaviour at a cooling rate of 64°/min are given in Table 9.

TABLE 9

Material	Relative Viscosity	T <sub>c</sub> °C	T <sub>p</sub> °C
(a)	61.5	163	154
(b)	80.3	164	153
(c)	74.4	171	161

## EXAMPLE 8.

Granules of nylon 6 (having a relative viscosity of 40), and a copolymer of nylon 66/6 (97/3 weight percent, relative viscosity 45) containing cyclohexyl phosphonic acid and zinc stearate in quantities to give 12.2  $\mu$

mole/g phosphorus and 7.9  $\mu$  mole/g zinc were extruded and the crystallization behaviour of the polymers determined at a cooling rate of 16°C/min. The results are given in Table 10 compared with control samples not containing the zinc stearate or phosphonic acid.

TABLE 10

Polymer	T <sub>c</sub> °C	T <sub>p</sub> °C
Nylon 6	207	191
Nylon 6 control	191	182
Nylon 66/6	240	230
Nylon 66/6 control	231	220

## EXAMPLE 9.

Granules of 66 nylon polymer containing 0.15% by weight TiO<sub>2</sub> and 0.25% by weight cyclohexyl phosphonic acid (15.2  $\mu$  mole P/g) were tumble blended with zinc stearate, ethylene-bis-stearamide and 66 nylon to give a series of compositions of varying cyclohexyl phosphonic acid content, each containing 0.5% by weight zinc stearate and 0.2% by weight ethylene bis-stearamide. These mixtures were extrusion compounded to give granular products. The fast cycling properties of each of these products were studied using a "Stübbe" SKM1-S injection

moulded machine fitted with a single-impression mould. ("Stübbe" is a registered Trade Mark). The times required to cool the mould to a temperature at which the moulded article could be removed from the mould without distortion of the moulding occurring was measured for each product. In all cases a constant injection time (time allowed for filling the mould) of 1.2 seconds was used. The cooling times are recorded below together with details of the crystallisation behaviour and mechanical properties of some of the blends.

TABLE 11

P $\mu$ mole/g	Cooling Time seconds	T <sub>c</sub> (°C) qc = 16°C/min	T <sub>p</sub> °C	Tensile Strength (MN/m <sup>2</sup> )	Flexural Modulus GN/m <sup>2</sup>
15	0.6	248	238	94	2.85
3.75	0.6	—	—	—	—
2.25	0.6	—	—	—	—
1.5	0.6	—	—	—	—
0.75	0.6	—	—	94	2.78
0.15	0.6	—	—	—	—
0.075	0.8	241.5	232.5	—	—
0.037	2.5	237.5	230.5	94	2.79
0.015	5.0	—	—	—	—
0	5.0	235	228	82	2.5

The control material differed from the above products in that it contained no cyclohexyl phosphonic acid and 0.3% by weight of zinc stearate.

5

#### EXAMPLE 10.

The procedure of Example 9 was repeated to give granular products containing varying

levels of zinc stearate, each containing 2.25  $\mu$  mole phosphorus/g in the form of cyclohexyl phosphonic acid and 0.2% ethylene-bis-stearamide. The fast cycling properties were evaluated using the procedure and the control sample used in Example 9 and the results obtained are recorded in Table 12.

.10

TABLE 12

Zinc stearate (% by weight)	Zinc ( $\mu$ mole./g)	Cooling Time (secs)
1	16	0.6
0.5	8	0.6
0.1	1.6	0.6
0.01	0.16	0.8
0		5.0

#### EXAMPLE 11.

The procedure of Example 9 was used to evaluate a series of different metal salts. Granular products were prepared containing 2.25  $\mu$  mole phosphorus/g (as cyclohexyl

20

phosphonic acid), 0.2% by weight of ethylene bis-stearamide and 8  $\mu$  equiv. m/g (where m is the metal) using the salts listed in Table 13.

TABLE 13

Additive	Cooling Time (seconds)
Calcium stearate	0.6
Magnesium stearate	0.6
Aluminium stearate	1.0
Lead stearate	0.8 — 1.0
Zinc stearate	0.6
Zinc oxide	0.6
Control	5.0

The control was that used in Example 9.

#### EXAMPLE 12.

Samples of nylon 66 (relative viscosity 45) were tumble blended with 0.5% by weight (7.9  $\mu$  mole/g) of zinc stearate and 0.1% by weight of phenyl phosphonic acid, phenyl phosphonic dichloride and dimethyl phenyl

30

phosphonate respectively. The three samples were extrusion compounded in a screw extruder under melt conditions at a temperature of 285°—290°C. The crystallisation behaviour of the products, determined as previously described, are recorded in Table 14.

35



TABLE 14

Phosphorus compound	P $\mu$ mole/g	T <sub>c</sub> (°C) q <sub>c</sub> = 16°C/min	T <sub>p</sub> (°C)
phenyl phosphonic acid	6	243.5	234
phenyl phosphonic dichloride	5	244.5	234.5
dimethyl phenyl phosphonate	5	244	233.5
Control (no additives)	0	235	227

## EXAMPLE 13.

5 Nylon 6 containing 0.25% by weight of cyclohexyl phosphonic acid was extrusion compounded in various proportions with batches of the same nylon 6 containing 0.5% by weight of zinc stearate to give blends containing the concentration of ingredients listed below.

Similar compositions were prepared by direct addition of various quantities of cyclohexyl phosphonic acid to the stearate-containing polymer followed by tumble blending and extrusion under melt conditions. Table 15 shows the crystallisation behaviour and mechanical proportions of the resultant products.

10

15

TABLE 15

P $\mu$ mole/g	T <sub>c</sub> (°C) q <sub>c</sub> = 16°C/min	T <sub>p</sub> (°C)	Tensile Strength MN/m <sup>2</sup>	Elongation to break (%)	Flexural Modulus GN/m <sup>2</sup>	Impact Strength (kJ/m <sup>2</sup> )
0.75*	183	166	85	12	2.31	27
0.3*	181	166	87	12	2.38	25
3 <sup>+</sup>	183	166	86	12	2.39	27
1.8 <sup>+</sup>	181	166	85	12	2.38	28
0.6 <sup>+</sup>	179	165	85	12	2.38	26
Control <sup>≠</sup>	170	159	72	36	2.10	41

\* present in nylon masterbatch

+ added direct to nylon by dry tumble blending

≠ containing only zinc stearate, no phosphorus

## EXAMPLE 14.

20 A nylon 66:nylon 6 copolymer containing the comonomers in the weight ratio 80:20 was extrusion compounded with 0.5% zinc stearate and 0.2% ethylene bis-stearamide. A sample of this material was tumble blended

with 0.2% by weight of cyclohexylphosphonic acid (12  $\mu$  mole/g) and the mixture was extrusion compounded. Table 16 shows the effect on the crystallisation and mechanical properties of the original blend of introducing the phosphonic acid.

25

TABLE 16

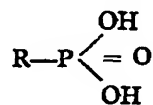
P $\mu$ mole/g	T <sub>c</sub> (°C) q <sub>c</sub> = 16°C/min	T <sub>p</sub> (°C)	Tensile Strength MN/m <sup>2</sup>	Elongation to break (%)	Flexural Modulus GN/m <sup>2</sup>	Impact Strength (kJ/m <sup>2</sup> )
0	198	189	68	100	1.67	29
12	213.5	198	76	22	1.97	22

## EXAMPLE 15.

Granules of nylon 66 (relative viscosity 45) containing 0.1% by weight of benzyl phosphonic acid was dry tumbled with 0.5% by weight of zinc stearate. The mixture was extrusion compounded at a temperature of 285—290°C as described in Example 1. The product was vacuum dried at 90°—100°C for 16 hours and the crystallisation properties of the composition were examined as described above. Values of  $T_g$  and  $T_p$  (measured at a cooling rate of 16°C/min) of 245.5°C and 234.5°C respectively were obtained. These compare with values of 235 and 228°C for the control polyamide not containing the combination of metal salt and benzyl phosphonic acid.

## WHAT WE CLAIM IS:—

1. A method of producing a polyamide composition comprising intimately blending an organophosphonic acid or derivative thereof as hereinbefore defined of general formula



where R is hydrocarbonyl radical and a metal compound which is a metal salt of a saturated or unsaturated carboxylic acid, a metal oxide or hydroxide with a polyamide under melt conditions wherein the metal is selected from Groups 2a, 2b, 3b, 4b, 7a and 8 of the Periodic Table of Elements (as tabulated on page 30 of Advanced Inorganic Chemistry by Cotton and Wilkinson published in 1962 by Interscience Publishers) and wherein either the metal compound or the organophosphorus compound, but not the combination of both compounds, may have been present during the polymerisation of the polyamide.

2. A method according to Claim 1 in which either the metal compound or the organophosphorus compound is intimately dispersed in a polyamide prior to the addition of whichever compound is not present in the polyamide.

3. A method according to Claim 1 or 2 in which both the metal compound and the organophosphorus compound are each intimately dispersed in separate batches of the polyamide before melt blending the batches of polyamide.

4. A method according to any one of Claims 1 to 3 in which R is selected from cycloaliphatic or aromatic radicals.

5. A method according to any one of Claims 1 to 4 in which R is selected from phenyl, benzyl and cyclohexyl radicals.

6. A method according to any one of Claims 1 to 5 in which the concentration of organophosphonic acid is such as to give between 0.025 mole and 120 mole of phosphorus per 10<sup>6</sup> gram of the polyamide composition.

7. A method according to Claim 6 in which the concentration of phosphorus is between 0.15 mole and 20 mole per 10<sup>6</sup> gram of polyamide composition.

8. A method according to any of Claims 1 to 7 in which the concentration of metal compound present is such as to give between 0.025 mole and 120 mole of metal per 10<sup>6</sup> gram of the polyamide composition.

9. A method according to Claim 8 in which the concentration of metal is between 0.15 mole and 20 mole per 10<sup>6</sup> gram of polyamide composition.

10. A method according to any one of Claims 1 to 9 in which the metal is selected from Groups 2a, 2b, 3b and 7a of the Periodic Table as hereinbefore defined.

11. A method according to any one of Claims 1 to 10 in which the metal compound is selected from salts of acetic, stearic and oleic acids.

12. A method according to any one of Claims 1 to 11 in which the polyamide is a polymer of nylon 6, nylon 66 or a copolymer of nylon 6/66.

13. A method according to any one of Claims 1 to 12 in which at least one of a delustrant, brightening agent, stabiliser, filler or toughening agent is intimately blended into the polyamide composition.

14. A method according to Claim 1 as hereinbefore described and with reference to the accompanying Examples.

15. A polyamide composition whenever obtained by a method as claimed in any one of Claims 1 to 14.

16. A polyamide composition according to Claim 15 containing a nucleating quantity of the mixture of metal compound and the organophosphorus compound having a crystallisation peak temperature (as hereinbefore defined) measured at a cooling rate of 16°C/min of at least 2°C higher than the same composition not containing the nucleating mixture.

17. Shaped articles in the form of a granules, fibre, film or moulded article comprising a polyamide composition according to either of Claims 15 or 16.

J. M. DOWNER,

Agent for the Applicants.

Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act, 1949, to patent No. 1,084,325.